"Zonal Effect" in the Slow Coagulation of Colloid Arsenious Sulphide.

By Shridhar Sarvottam JOSHI and Sadashiv S. KULKARNI.

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The results of numerous viscosity measurements reported in previous publications[1] suggested that the progress of a slow coagulation, contrary to the mechanism contemplated in Smoluchowski's classical theory,[2] for the kinetics of coagulation is not time continuous but zonal. Subsequent work on the behaviour of colloid manganese dioxide studied by the familiar opacity method[3] and that dependent on the determination of μ_D the refractivity[4] during numerous coagulations has confirmed the above deduction. That this zonal effect in slow coagulations is not merely an instance of the somewhat abnormal behaviour of colloid MnO_2,[5] but obtains more widely, is shown by results on the electrolytic coagulations of aqueous sodium oleate[4e] and different oil suspensions[4g] on the coagulations of other systems. Similar results are obtained with colloidal solutions of gold, antimony trisulphide and ferric oxide, which will be published shortly. The present paper reports the occurrence of the zonal effect in colloid As_2S_3.

Experimental. The colloid was prepared and its strength estimated as described by Joshi and Kulkarni.[4a] The course of coagulation was followed by measuring the variation of μ_D the refractive index for the sodium line by means of a Pulfrich refractometer. The general experimental procedure, the precautions observed during these measurements

(1) Joshi and Viswanath, *J. Indian Chem. Soc.*, **10** (1933), 329; Joshi and Menon, *ibid.*, **10** (1933), 599; Joshi and Nanjappa, *ibid.*, **11** (1934), 133; Joshi and Iyengar, *ibid.*, **11** (1934), 55, 573; Joshi and Panikkar, *ibid*, **11** (1934), 797; *J. chim. phys*, **32** (1935), 455; *Proc. Acad. Sci.* (United Provinces Agra Oudh, India), **5** (1935), 41.

(2) Smoluchowski, *Z. physik. Chem.*, **92** (1917), 129.

(3) Joshi and Purushottam, *Current Sci.*, **4** (1936), 870; Joshi and S. J. Rao, *J. Indian Chem. Soc.*, **13** (1936), 311.

(4a) Joshi and Kulkarni, *ibid.*, **13** (1936), 441.

(4b) Joshi and S. J. Rao, *ibid.*, **13** (1936), 141.

(4c) Joshi and Panikkar, *ibid.*, **13** (1936), 309.

(4d) Joshi and S. J. Rao, *Kolloid-Z.*, **76** (1936), 145.

(4e) Joshi and S. J. Rao, *Fettchem. Umshau*, **43** (1936), 36.

(4f) Joshi and Purushottam, *Current Sci.*, **4** (1936), 481.

(4g) Joshi and Sarkar, *J. Bombay Univ.*, **4** (1935), 140.

(5) Joshi and T. S. Narayan, *Kolloid-Z.*, **49** (1932), 335; *J. Indian Chem. Soc.*, **7** (1930), 883; Joshi and V. L. Narayan, *ibid., Sir P. C. Ray Comm. Vol.*, 1933, p. 41.

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have been described previously.[4b] The measurements were continued until the coagulating mixture in the refractometer cell remained sensibly homogeneous, that is, free from local and random turbidities due to the coagulam. Although a large number of coagulations were studied in regard to change of μ_D, only two μ_D-time curves are shown in Fig. 1 to indicate the generality of the results. The coagulant used was a suitably

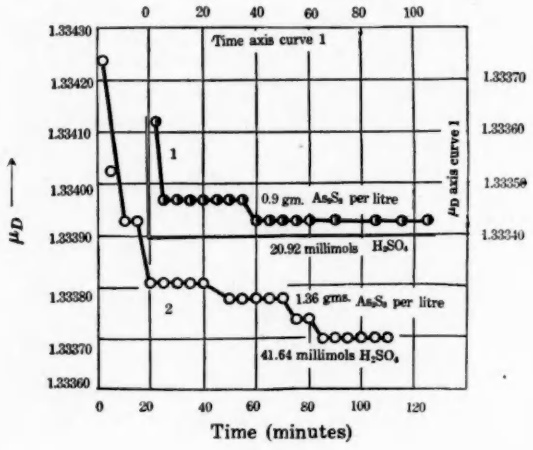

Fig. 1.

diluted solution of H_2SO_4, so as to produce a measurable change in μ_D during a moderate period. The concentration of the coagulant and of the colloid as indicated in Fig. 1 refer to their values in the coagulating mixture. The temperature was maintained constant at $25° \pm 0.1°$. The least changes in μ_D refer to 0.5 minute, which could be definitely measured with the instrument, and which corresponds to a change of about 0.00004 in μ_D.

Discussion. The two typical curves in Fig. 1 show definitely that the progress of coagulation as recorded by change of μ_D is not time-continuous, but discontinuous or zonal. It was observed that for a given concentration of the colloid, the net change in μ_D during the coagulation and the number of discontinuities or the zonal effect tends to diminish for very large and small values of the concentration of the coagulant. Similar, though not indentical is the influence of the change of colloid content at constant concentration of the coagulant. This is in complete accord with the results obtained previously.[1] It was observed, for

example, that a viscosity-time curve corresponding to a moderately high concentration of the coagulant showed a slight initial fall and then a continuous rise. With a lower concentration, the coagulation curve consisted of a definitely greater number of breaks or discontinuities. A satisfactory theory for the refractivity of a colloid is fundamental to the elucidation of the turbidity phenomena, which are the chief characteristic (for evidence indicating limitation of the validity of this familiar notion, compare Joshi and Kulkarni[4a]) of the coagulation phenomena; it must analyse the influence of such factors as the micellar charge, the nature of the surrounding Helmholtz layer, the refractivity of the continuous and the micellar material, the size and perhaps the shape of the particles; these determine the magnitude of the path in unit time of a light beam passing through the system, and therefore, its refractivity. These quantities are manifestly subject to change during coagulation. During the process, the coalescence of the particles increases the proportion of the medium viz. water in the light path. μ_D is expected to approach its value and therefore, diminish, since the refractivity of the dispersed material is ordinarily greater than that of water. That this change, concomitant with coagulation proceeds zonally is an interesting and hitherto practically an ignored feature of the phenomenon of coagulation in the slow region, and observed perhaps for the first time in colloid arsenious sulphide which has had about the longest and widest usage in studies of the coagulation phenomena.

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Études de l'effet du champ électrique sur la viscosité des liquides. I.

Par Osamu KIMURA.

(Reçu le 15 mars 1937.)

La viscosité d'un liquide est en général remarquablement influencée par des facteurs qui se rapportent à sa structure intérieure tels que la forme et la grandeur des molécules qui composent ce liquide et l'association de ces molécules, aussi bien que par l'attraction mutuelle entre ces molécules. Comme il en est ainsi, si l'on peut en changer volontairement sa structure intérieure par un certain champ de force, on trouvera

certainement le changement de la viscosité dû à ce champ appliqué. Il sera très intéressant d'utiliser ce changement pour étudier sa structure intérieure.

Quand on place un liquide polaire dans le champ électrique, ces molécules qui sont de forme allongée, auront une tendence à se diriger vers la direction du champ susdit, et sa structure intérieure changera, et par conséquent la viscosité le sera aussi. De ce point de vue, R. Herzog et ses collaborateurs[1] ont récemment étudié quelques solvants organiques, et A. Passynski[2] la solution benzénique de caoutchouc. Mais, on pourrait dire que leurs expériences ne seraient pas suffisantes pour comprendre la relation entre le changement de viscosité et la structure intérieure du liquide. Pour comprendre mieux, on a besoin de choisir une substance plus simple et de mesurer la viscosité plus précisément. Pour cette raison, j'ai construit un viscosimètre spécial, au moyen duquel on peut mesurer exactement la viscosité du liquide sous le champ électrique. Et j'ai choisi ici comme solvant le benzène qui est non polaire, et comme corps dissous l'acide stéarique dont la molécule a assez de longueur, en possédant un groupe polaire. Dans cet appareil le liquide s'écoule entre deux plaques-électrodes séparées de 0.2 mm. La direction du champ électrique est perpendiculaire à celle du courant de liquide.

Les résultats obtenus sont représentés dans le tableau et dans la figure, où on porte en abscisses les tensions électriques et en ordonnées les durées d'écoulement qui sont proportionnelles à la viscosité. La concentration de la solution était de 5%, et la température était 27.0° durant nos expériences.

Tableau 1.

Durée d'écoulement en secondes.	Intensité du champ en volts
47.4	0
47.6	4500
47.8	8750
48.1	13750
48.2	20000
48.2	25000
48.2	30000

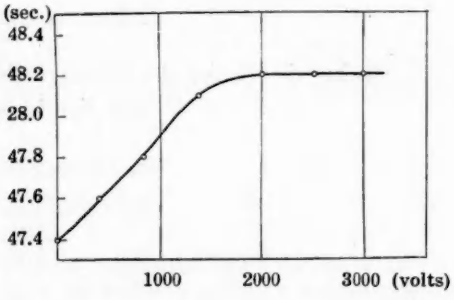


Fig. 1.

(1) R. Herzog, H. Kuder, et E. Paersch, *Physik. Z.*, **35** (1934), 446.
(2) A. Passynski, *Kolloid-Z.*, **70** (1935), 180.

Dans la figure on voit que, durant que la tension n'est pas encore grande, la viscosité s'augmente graduellement au fur et à mesure de l'accroissement de la tension, mais la viscosité arrive à un état de saturation, en n'y changeant plus sa valeur pour la variation de la tension. Pour comprendre mieux cet événement, j'ai essayé un calcul simple.

Si l'on indique par μ le moment électrique de l'acide stéarique et par F l'intensité du champ électrique, on peut calculer, selon la loi de Maxwell-Boltzmann, le nombre des molécules f qui font un angle α avec la direction du champ et un angle solide entre Ω et $\Omega+d\Omega$; donc on a:

$$f = Ae^{\frac{\mu F}{kT}\cos\alpha}\, d\Omega\,.$$

Comparons maintenant la valeur de μF à celle de kT, afin de trouver la relation qui existe entre l'agitation thermique moléculaire et le champ électrique appliqué. Si on pose le moment électrique de l'acide stéarique $= 1.8 \times 10^{-18}$ E.S.U., et la tension F la plus haute dans cette expérience $= 30{,}000$ volt/cm. $(= 100$ E.S.U.), on obtient

$$\frac{\mu F}{kT} = \frac{1.8\times10^{-18}\times100}{300\times1.37\times10^{-16}} = 4.4\times10^{-3}\,.$$

où $k = 1.37 \times 10^{-16}$, et $T = 300$.

On voit que la valeur de μF est beaucoup plus petite que celle de kT. Cela signifie que les molécules qui se dirigent parallèlement à la direction du champ ne sont pas encore nombreux. A la première vue, il semble que la viscosité doive s'augmenter proportionnellement à l'élévation de la tension, mais il n'en est pas ainsi. Elle atteint déjà à l'état de saturation pour une tension pas si grande. Il est très naturel de supposer que cette anomalie soit peut-être due à l'association de molécules de l'acide stéarique. Je ferai un rapport sur ce point dans le prochain mémoire.

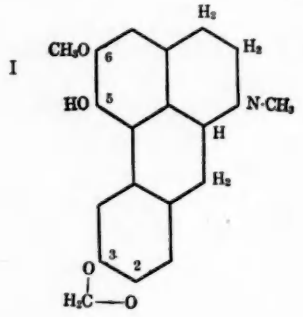
Ce travail a été effectué aux laboratoires de Chimie Colloïdale de l'Institut Shiomi et de l'Université Impériale d'Osaka. Tous mes remerciements sont dus à M. le Prof. N. Sata qui n'a pas cessé de s'intéresser très activement à mon travail et de donner tant de renseignements précieux.

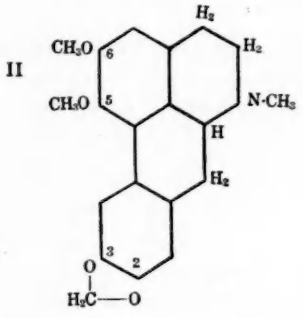
Synthese des Domesticin-äthyläthers.

Von Hideo SHISHIDO.

(Eingegangen am 23. März 1937.)

Die Konstitution von Domesticin[1] ist früher als eine Phenolbase (I) des *d*-Epidicentrins (II), welchem das Methoxyl in der 5-Stellung durch ein Hydroxyl ersetzt ist, angesprochen worden.[1] Zu dieser Vorstellung könnte man einen Beweis dadurch erbringen, dass man seinen

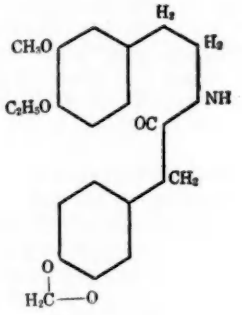


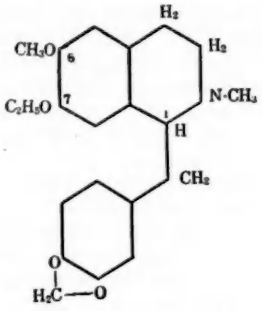


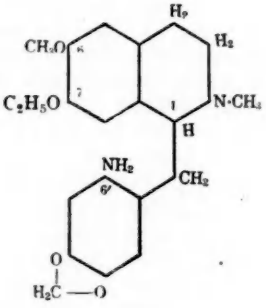
Äthyläther, i.e. Domesticin-äthyläther (VI), in der Weise synthetisiert,[2] dass in der Domesticin-methyläther-synthese[3] statt Veratrumaldehyds Äthylvanillin angewandt wird.

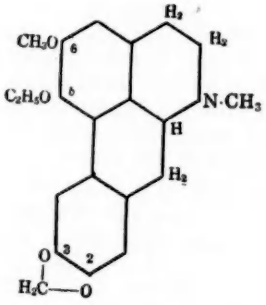
Zunächst wurde β-(3-Methoxy-4-äthoxy-phenyl)-äthyl-3′,4′-methylendioxy-phenacetamid (III) (Schmp. 115°) aus 3-Methoxy-4-äthoxy-β-phenyl-äthylamin und Homopiperonylsäure dargestellt. Dieses Amid wurde dann durch Phosphoroxychlorid in ein Dihydroisochinolinderivat übergeführt, mit Jodmethyl an seinem N methyliert, und durch Reduktion in eine Tetrahydro-verbindung (IV) (Schmp. 106°) umgewandelt. Diese letztere wurde schliesslich mit Salpetersäure an der 6′-Stellung nitriert, dann durch Reduktion mittels Stannochlorids und Salzsäure in eine 6′-Amino-verbindung (V) (Schmp. 90–92°) übergeführt, und diese unter Ringschluss zu inaktivem 2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin (VI) (Schmp. 132°) diazotiert. Dieses racemische

(1) Z. Kitasato, *Acta Phytochim.* (Japan), **3** (1927), 187.
(2) *Ibid.*, **9** (1937), 265.
(3) *Ann.*, **527** (1937), 176.

III 

IV 

V 

VI 

Produkt wurde nun mittels der *d*- und *l*-Weinsäure in beide aktive Komponenten gespaltet.

Die so synthetisch erhaltene *d*-Base schmolz bei 131°, zeigt $[\alpha]_D^{14} = +110.8°$ und ergibt keine Erniedrigung des Schmelzpunktes bei der Mischprobe mit dem natürlichen Domesticin-äthyläther.[4]

Beschreibung der Versuche.

β-(3-Methoxy-4-äthoxy-phenyl)-äthyl-3′, 4′-methylendioxy-phenacetamid (III). 36 g. Homopiperonylsäure werden mit 39 g. 3-Methoxy-4-äthoxy-β-phenyläthylamin[5] zwei Stunden am Rückflusskühler auf 180–190° erhitzt. Nach dem Erkalten wird das

(4) *Acta Phytochim.* (Japan), **9** (1937), 265.

(5) Zuerst wird 3-Methoxy-4-äthoxy-zimtsäure (Schmp. 199°) durch katalytische Reduktion (Palladium-Kohle) zu 3-Methoxy-4-äthoxy-phenylpropionsäure (Schmp. 132°) reduziert und dann wird diese in Chloroformlösung mit Thionylchlorid behandelt. Nach dem Stehen über Nacht wird die Lösung in ein Gemisch von Natronlauge und konz. Ammoniak eingegossen. Beim Verdunsten von Chloroform scheiden sich die Krystalle von 3-Methoxy-4-äthoxy-phenylpropionsäureamid ab (Schmp. 121°) (Gef.: C, 64.84; H, 7.90. Ber. für $C_{12}H_{17}O_3N$ (223): C, 64.57; H, 7.62%.). Dieses Säureamid wird dann durch Natriumhypochlorit in Äthylamin übergeführt.

krystallinische Reaktionsgemisch in 200 c.c. Chloroform gelöst und die Chloroformlösung je dreimal mit verdünnter Natronlauge und verdünnter Salzsäure und dann zweimal mit Wasser geschüttelt. Nach dem Trocknen mit festem Kaliumhydroxyd wird das Chloroform abgedampft und der Rückstand aus Benzol umkrystallisiert. Prismen vom Schmp. 114–115° (Ausbeute 42 g.). (Gef.: C, 67.08; H, 6.72. Ber. für $C_{20}H_{23}NO_5$ (357): C, 67.23; H, 6.44%.)

1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin (IV). 30 g. obiges Amid (III) werden mit 150 c.c. Toluol und 60 c.c. Phosphoroxychlorid anderthalb Stunden bei 130–140° gekocht. Nach dem Erkalten wird das Toluol mit Petroläther verdünnt und nach einigen Minuten wird die obenstehende Flüssigkeit abgegossen, und der krystallinische Rückstand mit Petroläther gut gewaschen und mit 150 c.c. Benzol, 300 c.c. Wasser und 10 c.c. konzentrierter Salzsäure unter Erwärmen auf dem Wasserbad vermischt. Nach Trennung der heissen Benzolschicht, wird die untere Schicht mit Natronlauge stark alkalisch gemacht und mit Benzol unter Zusatz von etwas Alkohol geschüttelt. Die Benzollösung wird mit Wasser gewaschen, mit Kaliumcarbonat getrocknet und nach dem Einengen mit 20 c.c. Jodmethyl gekocht. Das abgeschiedene rotbraune Öl erstarrt bald zu Krystallen. Nach 3–4-stündigem Kochen wird das Jodmethylat aus Alkohol umkrystallisiert. Prismen vom Schmp. 145° und Zersetzungsp. 155–157°. (Gef.: C, 52.23; H, 5.30. Ber. für $C_{21}H_{24}NO_4I$ (481): C, 52.39; H, 4.99%.)

Das obige Jodmethylat wird in Alkohol gelöst und mit einer genügenden Menge von dem neu gefällten Silberchlorid auf dem Wasserbad erhitzt. Dann wird das Reaktionsgemisch mit 800 c.c. Wasser auf dem Wasserbad bis zum vollständigen Verschwinden des Alkoholgruchs erwärmt. Das Filtrat vom Jodsilber wird bis auf 200 c.c. eingedampft, mit 50 c.c. 15%-iger Schwefelsäure versetzt und mit einem Überschuss von Zinkpulver auf dem Wasserbad reduziert. Das dabei gebildete schwer lösliche Sulfat wird unter Zusatz von Alkohol gelöst. Nach 5–6-stündigem Kochen wird die Lösung von Zinkpulver abfiltriert und der Alkohol abgedampft, wobei sich das Sulfat vollständig krystallinisch abscheidet. Das Sulfat wird in 50%-igem Alkohol gelöst und mit Ammoniak zersetzt. Das abgeschiedene Öl krystallisiert sofort in Prismen. Das so gewonnene 1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin wird dann aus Äthanol umkrystallisiert. Prismen vom Schmp. 105–106°. Ausbeute ca. 15 g. (Gef.: C, 71.22; H, 7.18. Ber. für $C_{21}H_{25}NO_4$ (355): C, 70.99; H, 7.04%.)

6′-Nitro-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin. Eine Lösung von 5 g. 1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin in 25 c.c. Eisessig wird mit 10 c.c. konzentrierter Salpetersäure unterhalb 5° nitriert. Nach 15 Minuten giesst man das Reaktionsgemisch in ein Gemisch von 300 c.c. gesättigter Ammoniumcarbonat-lösung und 200 g. Eis und sammelt nach 30 Minuten den abgeschiedenen Niederschlag und wäscht mit Eiswasser. Die so gewonnene Nitro-verbindung wird in 150 c.c. 3%-iger Salzsäure gelöst und mit Tierkohle 20 Minuten auf dem Wasserbad erhitzt. Nach dem Filtrieren macht man mit verdünntem Ammoniak unter Eiskühlung schwach alkalisch, saugt die Abscheidung ab, wäscht mit Wasser und trocknet auf der Tonplatte. Diese Substanz wird aus Alkohol und dann aus Benzol umkrystallisiert. Gelbe Prismen von Schmp. 178–179°. (Gef.: C, 63.33; H, 6.19. Ber. für $C_{21}H_{24}N_2O_6$ (400): C, 63.00; H, 6.00%.)

6′-Amino-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin (V). Die obige Nitro-verbindung (nicht umkrystallisiert) wird in 20 c.c. Eisessig gelöst und mit 10 g. Stannochlorid und 20 c.c. konzentrierter Salzsäure bei 35° reduziert.[6] Nach 12 Stunden wird das Reaktionsgemisch in 300 c.c. Wasser eingegossen und nach Zusatz von Kalilauge (70 g. KOH in 100 c.c. Wasser) dreimal mit Chloroform ausgezogen. Der Rückstand dieser Lösung wird in 10 c.c. Äthanol gelöst und mit einer Lösung von 1 g. Oxalsäure in 10 c.c. Äthanol versetzt. Das so erhaltene Oxalat schmilzt bei 193° unter Zersetzung. Ausbeute 3 g. Die Suspension dieses Oxalates in Kalilauge wird mit Äther ausgeschüttelt und der Abdampfungsrückstand der Ätherlösung wird aus Methanol umkrystallisiert. Lange Prismen vom Schmp. 96–98°. (Gef.: C, 68.38; H, 7.32. Ber. für $C_{21}H_{26}N_2O_4$ (370): C, 68.11; H, 7.03%.)

Das Mono-chlorhydrat wird auf übliche Weise dargestellt und aus methanolhaltigem Benzol umkrystallisiert. Prismen vom Schmp. 228° unter Zersetzung. (Gef.: C, 62.09; H, 6.94; N, 6.80. Ber. für $C_{21}H_{27}N_2O_4Cl$ (406.5): C, 61.99; H, 6.64; N, 6.89%.)

***d,l*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin (VI).** 6.5 g. 6′-Amino-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin-oxalat werden, wie bei der Synthese von Epidicentrin,[7] in 25 c.c. 10%-iger Schwefelsäure gelöst und mit 75 g. zerkleinerten Eisstücken versetzt, und zu diesem Gemisch 7.5 c.c. 2 N Natriumnitritlösung sehr langsam zugetropft. Nach etwa 30 Minuten wird die diazotierte Lösung mit Kupferpulver versetzt, wobei man Entwicklung von Stickstoff und die Farbveränderung der Flüssigkeit beobachtet. Nach 4 Stunden wird die vom Kupferpulver abfiltrierte Flüssigkeit unter Zusatz von Methanol mit 2.5 g. Zinkpulver und 7.5 c.c. konzentrierter Salzsäure auf dem kochenden Wasserbad 15 Minuten reduziert. Das Filtrat vom Zink wird mit Ammoniak alkalisch gemacht, mit Äther sechsmal ausgezogen und der Rückstand des Äthers in Methanol gelöst. Wird die Lösung mit wenig 20%-iger Salzsäure versetzt, so krystallisiert das Chlorhydrat der *d,l*-Base (VI) aus. Es färbt sich gegen 250° und schmilzt bei 275–277° unter Zersetzung. Ausbeute an Chlorhydrat ca. 15%. Es ist schwer löslich in heissem Wasser und Äthanol. (Gef.: C, 64.26; H, 6.63. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16%.)

Die Suspension des so dargestellten Chlorhydrats in Natronlauge wird mit Äther ausgeschüttelt, und die Ätherlösung mit Wasser gewaschen. Der Abdampfungsrückstand des Äthers wird aus Äthanol umkrystallisiert. Prismen vom Schmp. 132°. Sie sind leicht löslich in heissem Äthanol, Methanol und Chloroform, aber etwas schwerer in Äther. (Gef.: C, 71.72; H, 6.97. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.)

Spaltung der racemischen Base in optische Antipode. In eine Lösung von 1.6 g. der wie oben erhaltenen *d,l*-Base (VI) in 70 c.c. Äthanol werden 3.3 c.c. einer 2 N alkoholischen Lösung von *d*-Weinsäure hinzugefügt. Das gebildete *l*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin-*d*-tartrat wird nach 10 Minuten Stehen abfiltriert und mit Alkohol gut gewaschen. Das Tartrat wird aus Äthanol umkrystallisiert in Prismen vom Schmp. 237° unter Zersetzung. Es wird in warmem Wasser gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther aus-

(6) Vgl. *J. Chem. Soc.*, **127** (1925), 2018.
(7) *Ann.*, **527** (1937), 180.

geschüttelt. Der Rückstand der Ätherlösung wird aus Methanol umkrystallisiert. Feine Prismen vom Schmp. 129–131°. (Gef.: C, 71.95; H, 6.82. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.) $[\alpha]_D^{14} = -110.9°$ (in Methanol).

Das Chlorhydrat wird auf übliche Weise dargestellt und aus einem Gemisch von Methanol, Äther und Petroläther umkrystallisiert. Prismen vom Schmp. 257° unter Zersetzung. (Gef.: C, 65.01; H, 6.23. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16%.)

Die Mutterlauge sammt dem Wasch-Alkohol von *l*-Base-*d*-tartrat wird in Vakuum abgedampft, der Rückstand wird in Wasser gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther extrahiert. Der Rückstand des Äthers wird in 35 c.c. Äthanol gelöst und mit 4.6 c.c. einer N alkoholischen Lösung von *l*-Weinsäure versetzt. Man saugt die so abgeschiedenen Krystalle von *d*-Base-*l*-tartrat ab und wäscht mit Äthanol. Prismen vom Schmp. 237° unter Zersetzung. Man suspendiert sie in Natronlauge und nimmt die frei gesetzte Base mit Äther. Dann verdampft man den Äther und krystallisiert den Rückstand aus Methanol um, wobei man *d*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin (VI) in Prismen vom Schmp. 131° erhält. Es nimmt mit konzentrierter Schwefelsäure eine rotviolette Farbe an, die durch Salpetersäure-dampf ins Blaugrün umschlägt. Diese Farbenreaktion tritt auch bei Domesticin-äthyläther auf. Die Mischprobe dieser Base mit dem natürlichen Domesticin-äthyläther zeigt keine Erniedrigung des Schmelzpunktes.[8] (Gef.: C, 71.66; H, 6.81. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.) $[\alpha]_D^{14} = +110.8°$ (in Methanol).

Man erhält das Chlorhydrat auf übliche Weise und es krystallisiert aus einem Gemisch von Methanol, Äther und Petroläther in Prismen vom Schmp. 257° unter Zersetzung (es färbt sich gegen ca. 230°). Es ist identisch mit natürlichem Domesticin-äthyläther-chlorhydrat (Mischprobe). (Gef.: C, 64.88; H, 6.06; N, 3.53. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16; N, 3.59%.)

Natürlicher Domesticin-äthyläther. Es wurde nach der Angabe Kitasatos[9] dargestellt und krystallisiert aus Petroläther, Äther und dann aus Methanol in Prismen vom Schmp. 130–131° aus. (Gef.: C, 71.52; H, 6.84. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.)

Das Chlorhydrat wird aus einem Gemisch von Methanol, Äther und Petroläther umkrystallisiert. Es bildet Prismen, färbt sich gegen ca. 230° und schmilzt bei 257° unter Zersetzung. Es ist leicht löslich in gewöhnlichen Lösungsmitteln. (Gef.: C, 65.05; H, 6.55; N, 3.61. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16; N, 3.59%.)

Zum Schluss möchte ich Herrn Dr. Zenjiro Kitasato für seine freundliche Leitung und gütige Unterstützung meinen herzlichsten Dank aussprechen.

Chem. Laboratorium des Kitasato-Institut, Tokyo.

(8) *Acta Phytochim.* (Japan), **9** (1937), 265.
(9) *Ibid.*, **3** (1927), 202; **9** (1937), 265.

Studies on the Raman Effect of Organic Substances. VIII. Raman Effect of Furane Derivatives.

By Kichimatsu MATSUNO and Kwan HAN.

(Received April 5th, 1937.)

Introduction. In our two previous papers,[1][2] investigations on the Raman spectra of ethyl cinnamate and ethyl α-furfuracrylate were described. In the present investigation, the Raman spectra of methyl and ethyl esters of the so-called stable α-furfuracrylic acid, *trans*-cinnamic acid, and the reduced products, viz., α-furylpropionates and hydrocinnamates, have been taken, in order to study the relation between the Raman spectra and the isomerism.

Experimental. The substances used were synthesized by the following processes: Methyl α-furfuracrylate (I) (m.p. 26.5°, b.p. 96°/3 mm.) and ethyl α-furfuracrylate (II) (b.p. 114°/3 mm.) were prepared by treating the mixtures of the silver salt of stable α-furfuracrylic acid, F-CH:CH·COOH* (m.p. 140°) and the corresponding alkyl iodides.

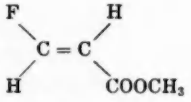
trans-Methyl cinnamate (III) (m.p. 34°, b.p. 127°/10 mm.) and *trans*-ethyl cinnamate (IV) (b.p. 136°/10 mm.) were obtained by treating Kahlbaum's cinnamic acid (m.p. 133°) and the corresponding alcohols in the presence of concentrated sulphuric acid, according to the method of Fischer and Speier.[3]

Methyl α-furylpropionate (V) (b.p. 67°/3 mm.) and ethyl α-furylpropionate (VI) (b.p. 74°/8 mm.) were obtained by reducing the corresponding α-furfuracrylate, F-CH:CH·COOR, with 2.5% sodium amalgam in alcohol solution in the presence of acetic acid. The reduction was repeated until the intense Raman line at $\Delta\nu$ 1640 cm.$^{-1}$ in the Raman spectra, associated with the C:C bond, disappeared.

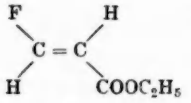
Methyl hydrocinnamate[4] (VII) (b.p. 105°/8 mm.) and ethyl hydrocinnamate[4] (VIII) (b.p. 127°/15 mm.) were prepared by warming the

(1) This Bulletin, **9** (1934), 88.
(2) *Ibid.*, **9** (1934), 327.
* F denotes α-furyl group in this paper.
(3) Fischer and Speier, *Ber.*, **28** (1895), 3254.
(4) Erlenmeyer, *Ann.*, **137** (1866), 334.

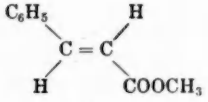
mixtures of hydrocinnamic acid (m.p. 48°) and the corresponding alcohols by the action of dry hydrogen chloride. All the substances were washed with the solution of sodium bicarbonate or sodium carbonate and finally with water. After dehydrating over calcium chloride and sucking off all the ether, the esters were distilled under reduced pressure. The middle fraction in the final distillation was employed in the investigation. The structural formulæ of the substances are as follows:



I



II



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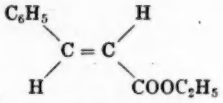

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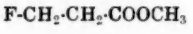

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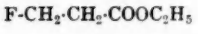
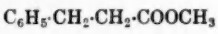
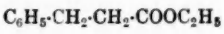


VI



VII



VIII

trans-Methyl cinnamate (m.p. 34°) is colourless crystals at room temperature, while *cis*-methyl cinnamate being a liquid (m.p. −3.5°) which agrees with the results obtained by Kistiakowsky and his co-worker.[5] The so-called stable methyl *α*-furfuracrylate is also colourless crystals (m.p. 26.5°). The ether solution (ca. 1/5 mol) of methyl furfuracrylate and methyl cinnamate were used in the experiments of the Raman spectra. After long exposure the solvent was removed off and the crystals identical with the *trans*-methyl cinnamate and methyl *α*-furfuracrylate were recovered.

The Raman spectra were taken by means of a spectrograph with three prisms,[2] using a saturated solution of sodium nitrite as a filter, in order to prevent the samples from the isomerization due to the action of the light in ultra-violet region. The numbers of the Raman lines (n), the numbers of the plates, and the conditions under which the spectra were taken, are summarized in Table 1. The results of the Raman spectra are shown in Table 2. Methyl cinnamate in the fused state and ethyl cinnamate have been studied by Kohlrausch and his co-worker.[6] The results are compared in Table 3.

(5) G. B. Kistiakowsky and Walter R. Smith, *J. Am. Chem. Soc.*, **57** (1935), 269.
(6) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **64** (1934), 374.

Table 1.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (°C.)	Time of exposure (hours)
Methyl α-furfuracrylate (I)	20	365	65	15	8
Ethyl α-furfuracrylate (II)	32	372	55	15	14
trans-Methyl cinnamate (III)	59	356	65	22	14
trans-Ethyl cinnamate (IV)	65	354	65	23	6
Methyl α-furylpropionate (V)	33	360	60	22	8
		361	65	21	14
Ethyl α-furylpropionate (VI)	23	366	65	15	8
Methyl hydrocinnamate (VII)	27	363	65	20	12
Ethyl hydrocinnamate (VIII)	25	359	65	23	8

Table 2. The $\Delta\nu$ Values of the Raman Spectra of Furane Derivatives.

(1) Methyl *α*-Furfuracrylate (I).

135 (2d); 384 (½d); 776 (4); 887 (2); 930 (1); 1023 (6); 1081 (3); 1160 (5); 1217 (5); 1268 (4); 1287 (5); 1396 (6); 1441 (2); 1485 (8); 1574 (2); 1644 (10); 1715 (5d); 3130 (3).

(2) Ethyl *α*-furfuracrylate (II).

761 (2); 794 (2); 817 (1); 862 (1); 887 (3); 934 (4); 978 (1d); 1021 (8); 1082 (4); 1160 (6); 1190 (2); 1212 (6); 1265 (5); 1283 (8); 1311 (½); 1334 (½); 1361 (1); 1389 (9); 1478 (10); 1575 (3); 1642 (10); 1704 (8d); 2928 (1d); 2976 (2); 3121 (2); 3151 (½).

(3) *trans*-Methyl cinnamate (III).

216 (1b, d); 360 (½); 576 (2); 616 (4); 718 (4); 769 (1d); 834 (3b); 861 (3); 933 (2b); 998 (8); 1028 (2b); 1158 (6b); 1179 (6b); 1201 (5); 1267 (4b, d); 1307 (3b, d); 1345 (2); 1443 (5d); 1494 (4); 1574 (4); 1597 (9b); 1634 (10b); 1713 (6b); 2841 (2b, d); 2875 (3b, d); 2963 (3); 3058 (1b, d).

(4) *trans*-Ethyl cinnamate (IV).

177 (2b, d); 279 (1b, d); 403 (2d); 475 (0); 571 (4); 616 (6s); 717 (4b, d); 740 (2); 775 (3); 836 (5); 867 (5d); 977 (1d); 996 (10s); 1025 (3); 1116 (3b, d); 1156 (3); 1178 (8); 1200 (8); 1259 (6d); 1303 (5d); 1331 (3); 1363 (3); 1392 (3); 1447 (5); 1494 (5); 1572 (3); 1597 (10); 1634 (10); 1706 (8); 2922 (3d); 2981 (3); 3067 (5d).

Table 2.—(*Concluded*)

(5) Methyl *α*-furylpropionate (V).

384 (½ d); 700 (½); 837 (1); 886 (2); 922 (½ d); 1019 (2); 1054 (1); 1078 (5); 1145 (4b, d); 1215 (3); 1388 (5); 1450 (1b, d); 1508 (10); 1599 (5); 1735 (2d); 2924 (2d); 2954 (3); 3118 (5); 3155 (2).

(6) Ethyl *α*-furylpropionate (VI).

699 (½); 858 (2); 882 (2); 922 (½); 1017 (1); 1050 (½); 1079 (4); 1118 (½); 1143 (2b); 1213 (3); 1387 (3); 1451 (2d); 1505 (8); 1597 (5); 1734 (2d); 2929 (3d); 2983 (2); 3126 (2); (3154) (3).

(7) Methyl hydrocinnamate (VII).

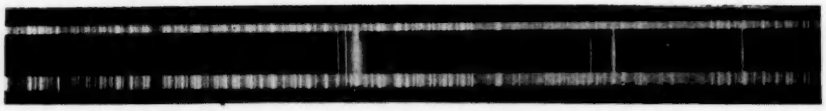
244 (2d); 424 (2d); 618 (5); 749 (1d); 759 (3); 837 (1d); 889 (3); 941 (2b); 997 (10); 1025 (5); 1178 (2); 1197 (5); 1443 (2d); 1578 (2); 1597 (6); 1630 (2); 1730 (3d); 2841 (1); 2917 (3b); 2945 (2d); 2997 (2); 3053 (3d).

(8) Ethyl hydrocinnamate (VIII).

374 (½); 618 (3); 767 (2); 859 (1); 999 (8); 1028 (4); 1105 (2d); 1174 (3); 1196 (6); 1261 (5); 1446 (2); 1589 (1); 1602 (6); 1724 (3d); 2926 (2d); 2970 (1); 3056 (5d).

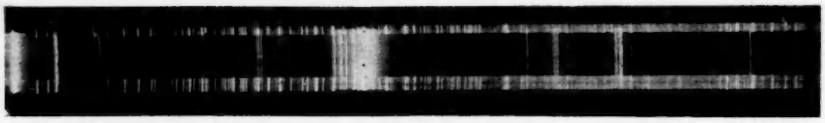
(1) Methyl α-furfuracrylate (I)

(2) Ethyl α-furfuracrylate (II)



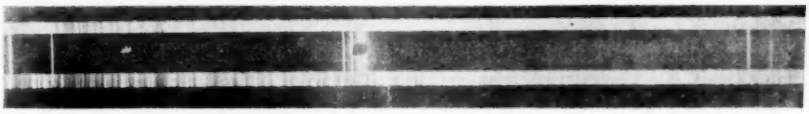
(3) *trans*-Methyl cinnamate (III)

(4) *trans*-Ethyl cinnamate (IV)



(5) Methyl α-furylpropionate (V)

(6) Ethyl α-furylpropionate (VI)



(7) Methyl hydrocinnamate (VII)

(8) Ethyl hydrocinnamate (VIII)

Discussion. In the previous papers,[1][2] one of the authors has shown that the Raman frequencies, ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm.$^{-1}$ are characteristic of the α-furfuryl-compounds, and the frequencies in the region between $\Delta\nu$ 1460 and 1600 cm.$^{-1}$ can be used as an indicator to distinguish α-furfuryl- from α-furfuridene or α-furoyl-compounds. In the present investigation, the frequencies of $\Delta\nu$ 1478, 1575, and 1642 cm.$^{-1}$ are found in α-furfuracrylates while 1505 and 1597 cm.$^{-1}$ are found in α-furylpropionates, as shown in Table 4. The appearance of $\Delta\nu$ 1642 cm.$^{-1}$ in the former but not in the latter cases is reasonable, for the appearance of a Raman shift, $\Delta\nu$ 1640 ± 20 is quite indicative of a double linkage in the side chain.

It has been observed that there is a considerable difference between the spectra of the *cis*- and *trans*-isomers.[7] Grédy[8] has investigated the Raman spectra of the *cis-trans*-isomers of cinnamic compounds and concluded that 1264, 1408, 1642, and 3021 cm.$^{-1}$ are found in the

(7) H. Hibben, *Chem. Rev.*, **18** (1936), 31.
(8) Blanche Grédy, *Compt. rend.*, **202** (1936), 664.

Table 3. Comparison of the Results on Cinnamates.

Methyl cinnamate		Ethyl cinnamate	
Kohlrausch	The authors	Kohlrausch	The authors
217	216	—	177
274	—	—	279
357	360	—	403
402	—	—	475
576	576	582	571
616	616	616	616
710	718	718	717
—	—	—	740
771	769	—	775
837	834	846	836
862	861	865	867
938	933	—	—
977	—	—	977
998	998	1004	996
1028	1028	1030	1025
—	—	—	1116
1165	1158	1163	1156
1181	1179	1185	1178
1201	1201	1201	1200
1268	1267	1264	1259
1311	1306	1303	1303
1336	1335	1324	1331
—	—	—	1363
—	—	—	1392
1447	1443	1446	1447
1495	1494	1496	1494
1578	1574	—	1572
1598	1597	1595	1597
1634	1634	1631	1634
1712	1713	1706	1706
2836	2841	—	—
2880	2875	2934	2922
2956	2963	2980	2981
3037	3058	3055	3067

Table 4.

C_6H_5·CH : CH-COOR		F-CH : CH-COOR		F-CH_2·CH_2·COOR	
R = CH_3	R = C_2H_5	R = CH_3	R = C_2H_5	R = CH_3	R = C_2H_5
718	717	—	—	700	699
—	740	—	—		
769	775	776	761	—	—
—	—	—	794	—	—
834	836	—	817	837	—
861	867	—	862	—	858
—	—	887	887	886	882
933	977	930	934	922	922
			978		
998	996	—	—	—	—
1028	1025	1023	1021	1019	1017
				1054	1050
—	—	1081	1082	1078	1079
—	1116	—	—	—	1118
1158	1156	1160	1160	1145	1143
1179	1178	—	1190	—	—
1201	1200	1217	1212	1215	1213
1267	1259	1268	1265	—	—
1306	1303	1287	1283	—	—
			1311		
1335	1331	—	1334	—	—
—	1363	—	1361	—	—
—	1392	1396	1389	1388	1387
1443	1447	1441	—	1450	1451
1494	1494	1485	1478	1508	1505
1572	1572	1574	1575	—	—
1597	1597	—	—	1599	1597
1634	1634	1644	1642	—	—
1713	1706	1715	1704	1735	1734

cis-forms, while 1209, 1274, and 1657 cm.$^{-1}$ in the *trans*-forms as shown in Table 5. The disappearance of $\Delta\nu$ 1408 and the appearance of 1201, 1306, and 1634 in the *trans*-cinnamates may give an evidence that a little transition from *cis*- to *trans*-forms takes place during the experiment of the Raman spectra under the filtered mercury light. It is likewise

possible to consider that the disappearance of 1408 and the appearance of 1190, 1212,[9] 1283, and 1642 cm.$^{-1}$ in furfuracrylates are attributable to the *trans*-forms of the esters.

Table 5. Some Raman shifts in the *cis*- and *trans*-isomers of cinnamic compounds observed by Grédy.[8]

C_6H_5·CH : CH·CH_3	*cis*		1264	1408	1642	3021
	trans	1210	1278		1665	
C_6H_5·CH : CH·CH_2OH	*cis*		1256	1408	1642	3022
	trans	1209	1274		1657	
C_6H_5·CH : CH·CH_2OCH_3	*cis*		1255	1410	1643	3025
	trans	1208	1278		1657	
C_6H_5·CH : CH·CH_2OCOCH_3	*cis*		1250	1412	1645	3032
	trans		1281		1659	
C_6H_5·CH : CH·CH_2Br	*trans*	1206	1282		1646	

It is doubtful, at a glance, that the important Raman shift associated with the C:C linkage has the values of $\Delta\nu$ 1634 in *trans*-cinnamates and 1642 cm.$^{-1}$ in *a*-furfuracrylates. But it is reasonable to consider that the shift questioned above is due to the effect of a conjugated double bond of carbonyl group, C:O. It is well-known that the C:C frequency is decreased by the effect of the conjugated double bonds. We may consider some other examples from the work of Hibben.[7]

Table 6. The Effect of Substitution on the C : C Shifts.

Radical R	CH_2 : CH-R	R-CH : CH-R	
		cis	*trans*
CH_3	1647		
CH_2OH	1646	1658	1677
C_nH_{2n+1} (n = 2–6)	1642	1658	1674
C_6H_5	1631	1642	1665
COOH	1638	1645	1652
COOR		1644	1655
CHO	1618	1625	1642
CN		1628	1645

(9) $\Delta\nu$ 1212 cm.$^{-1}$ is also attributable to the furane ring.

It is obvious that the carbonyl or the aromatic radical has an effect to decrease the C:C shift on account of the conjugated double bonds. Consequently, a remarkable decrease of the C:C shift will be expected in cinnamates and α-furfuracrylates which have the aromatic and the carbonyl radicals attached to the two sides of the ethylene linkage. The fact that $\Delta\nu$ 1634 cm.$^{-1}$ was found in stilbene[10] and $\Delta\nu$ 1640 cm.$^{-1}$ in diethyl fumarate[11] seems to make an other confirmation about it. If the *cis*- and *trans*-isomers were co-existent, other Raman lines, associated with the *cis*-compound, would be found at ca. $\Delta\nu$ 1620–1630 cm.$^{-1}$ besides the shift mentioned above. We may consider that the appearance of the intense lines at $\Delta\nu$ 1634 cm.$^{-1}$ in cinnamates and at $\Delta\nu$ 1642 cm.$^{-1}$ in the so-called stable α-furfuracrylates is attributable to the *trans*-form of the substances.

Summary.

(1) The Raman spectra of methyl and ethyl esters of α-furfuracrylic acid, cinnamic acid, α-furylpropionic acid, and hydrocinnamic acid have been measured.

(2) On comparing the Raman spectra of α-furfuracrylates with those of *trans*-cinnamates and other cinnamic compounds, the so-called stable furfuracrylates are considered as the *trans*-esters.

In conclusion, the authors are indebted to Ass. Prof. T. Nozoe for his valuable advice in the work of synthesis of the samples. The expense of this experiment was paid from a grant given by the Nippon Gakuzyutu Sinko Kwai, for which thanks are due.

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(10) Dadieu, Pongratz, and Kohlrausch, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. II a, **140** (1931), 353.

(11) Dadieu, Pongratz, and Kohlrausch, *ibid.*, **140** (1931), 647.

On the Silver Oxide Positive of the Alkaline Accumulator. I.

By Kyôji KINOSHITA.

(Received April 5th, 1937.)

The alkaline accumulator composed of the silver oxide positive and copper negative was already described by E. W. Jungner. The fundamental chemical reactions involved in the discharge of this accumulator are said to be the followings:

$$Ag_2O_2 + 2\,KOH + 2\,Cu = Ag_2O + 2\,KOH + Cu_2O \qquad (1),$$

$$Ag_2O + 2\,KOH + 2\,Cu = 2\,Ag + 2\,KOH + Cu_2O \qquad (2).$$

The terminal voltages of the cell corresponding to the reaction (1) and (2) were reported to be 0.93 volt and 0.65–0.7 volt respectively. In 1927 F. Jirsa[1] studied the cell of the form Ag/OH′/Fe. He prepared the silver oxide electrodes of the cell by pressing powdered silver oxide or iron on the suitable wire gauze.

The author prepared the silver oxide positive of the alkaline cell in powdered and in pasted forms, and made some experiments on this positive electrode. The present report is the abstract from the detailed description published in Japanese.[2]

Silver Oxide Positives Prepared in Powdered Form. At first the electrode was prepared by packing the powdered silver oxide (Ag_2O) into the pocket made of silver wire gauze. The size of the pocket was 9 cm. × 3.5 cm. × 2 cm. The cell was made by combining this positive with a negative electrode of a "Nife accumulator." The negative electrode, therefore, was composed principally of iron. The electrolyte used was 20% KOH solution.

The initial charge of the positive electrode was continued for about 20 hours by the current of 1 ampere. The open circuit voltage was found to be 1.260 volts. Eleven cycles of charge and discharge were undertaken and the results obtained are tabulated in Table 1. The characteristic curves of discharge are shown in Fig. 1, the number of cycle being indicated by the figure from 1 to 11.

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(1) Jirsa, *Z. Elektrochem.*, **33** (1927), 129.

(2) Kinoshita, *Toyoda Kenkyu Iho*, **3** (1935), 88; *ibid.*, **4** (1936), 96.

Table 1.

Number of cycles	Discharge current (milliamp.)	End point voltage (volts)	Discharge capacity (a. h.)
1	200–600	0.92	3.10
2	1000	0.0	5.42
3	1000	0.0	4.13
4	1000	0.0	3.43
5	1000	0.57	2.83
6	500	0.49	4.09
7	700	0.0	5.32
8	600	0.0	4.67
9	600	0.0	5.05
10	600	0.36	5.30
11	700	0.0	5.23

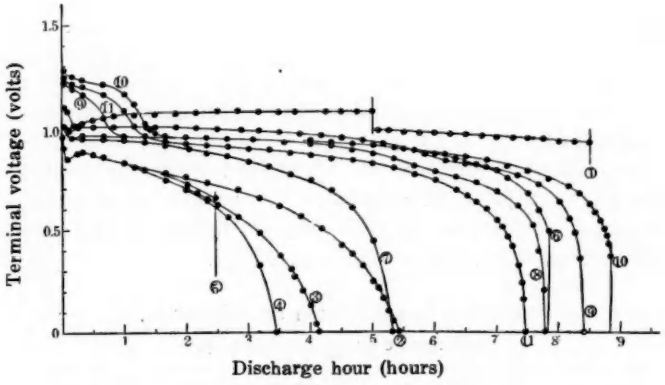

Fig. 1.

In the course of these experiments, as was already noticed by Jirsa, peptization of the active material of the positive electrode took place. As seen from Fig. 1 the forms of the curves for the last three cycles, i.e. 9, 10, and 11th cycle, differ remarkably from the other one. The terminal voltage of the cell falls in two steps, 1.2 volts and 1.0–0.9 volt, and then finally it drops to zero volt. This fact may be interpreted in the following manner.

The active material of the positive plate at the first discharge may be Ag_2O, but this will be then oxidized to Ag_2O_2 in the course of repetition of the cycles of charges and discharges. As the results of this electrolytic oxidation of the active material, the chemical reactions accompanied by the process of discharge may proceed in two stages as shown in the following equations.

$$Ag_2O_2 = Ag_2O + {}^1/_2\, O_2 \quad (3),$$

$$Ag_2O = 2\,Ag + {}^1/_2\, O_2 \quad (4).$$

The higher terminal voltage at the beginning is considered to be the result of reaction (3), and the lower terminal voltage reaction (4).

Silver Oxide Positives Prepared in Pasted Form. The experiments have been undertaken, then, on the silver oxide positives prepared in the pasted form. The powdered silver oxide was made into paste by mixing with NH_4OH or KOH solution and applied to the grid in the same manner as the ordinary pasted type electrodes of the lead acid cell. The grid was prepared by plating silver on the ordinary grid of lead-antimony alloy. The size of the grid was about 6.0 cm. × 1.5 cm. × 0.3 cm.

The paste was made by adding 1.7 c.c. of 20% KOH or 1.5 c.c. of 5N NH_4OH solution drop by drop to 10 g. of Ag_2O. After pasting the grids were left to dry in the room temperature for about 72 hours, and then were formed into the positives in 20% KOH solution by the current of 40–60 milliamperes.

The silver oxide positives thus prepared was combined with the Nife's negative in 20% KOH solution. The results of charges and discharges obtained on the positive electrode are tabulated in Table 2. The amount of Ag_2O pasted in this grid was 5.21 g.

Table 2. Results from an Electrode.

Discharge current 500 milliamp.

Number of cycles	Discharge capacity (a. h.)	Discharge capacity per 1 g. of Ag_2O. (m. a. h./g.)	Coefficient of utility (%)
1	2.285	439	94.8
2	1.642	315	68.1
3	1.666	320	69.1
4	1.576	303	65.4
5	1.642	315	68.1
6	1.616	310	67.0
7	1.576	303	65.4
8	1.542	296	64.0
9	1.550	298	64.3
10	1.550	298	64.3

The discharge current, in this case, was 500 milliamperes and the end point voltage of the cell was taken to be zero volt against Nife's negative. The 3rd column of Table 2 shows the capacities per one gram of Ag_2O, and the 4th column the percentage ratio of the actual capacity of the plate to the theoretical one. The theoretical capacity was calculated assuming the fundamental chemical reaction for discharge, for 4F of the electricity, to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

The ratio thus obtained may be considered to represent the coefficient of utility of the active material in the plate. As seen from this table very large discharge capacity was obtained at the first cycle of discharge, the utility coefficient of which amounting to 94.8%. From the 2nd cycle of discharge onwards the utility coefficient falls to about 60–70%.

This particularity of the 1st discharge was noticed in all silver oxide positives other than exemplified in Table 2.

Characteristic curves of the electrodes in charge and discharge are shown in Fig. 2, Fig. 3, and Fig. 4.

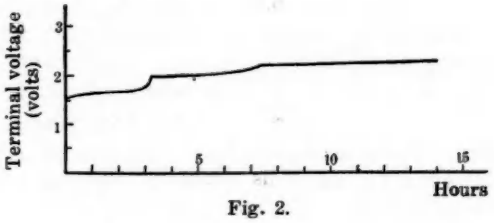

Fig. 2.

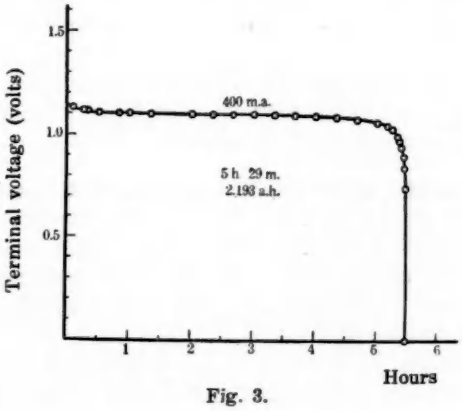

Fig. 3.

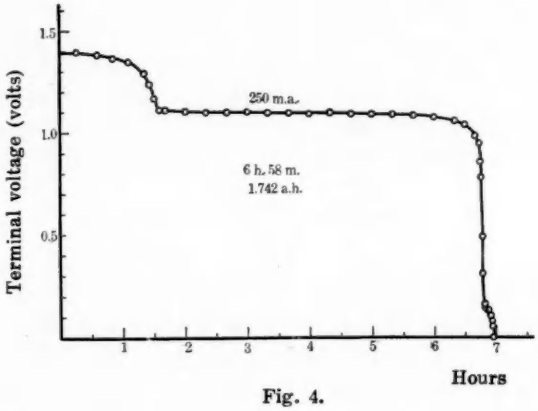

Fig. 4.

Fig. 2 is the charging curve of the positive electrode of a cell. The terminal voltage of this cell in charge rises abruptly at two points, namely at about 3.25 hours and 7.25 hours.

Fig. 3 and Fig. 4 show the discharge curves of another positive at the 1st discharge (discharge current 400 milliamperes) and the 8th discharge (discharge current 250 milliamperes) respectively.

At the first cycle of discharge, the silver oxide electrode always shows a curve of the form like Fig. 3. After repeating a few cycles of discharge the curve transforms to the form like Fig. 4. An overcharged Nife's negative was always used as the auxiliary electrode for the measurement of the terminal voltage of the electrode.

The above described change of form of the discharge curve, therefore, is considered to be due to the special feature of the silver oxide electrode.

The form of the discharge characteristic curve shown in Fig. 4 may be understood by considering that the fundamental chemical reactions (3) and (4) are involved in the electrode.

Comparison of the Silver Oxide Electrode with Lead Peroxide Positives. As already shown in Table 2 the utility coefficient of the silver oxide positive amounts to extraordinary high value in comparison with that of the positive of the lead acid cell. The coefficient of utility of the positive electrode of the lead acid cell is said to be about 25%–50% in 5 hour rate of discharge.

The capacities per 1 gram of the active materials of silver oxide and lead peroxide electrodes are plotted against the magnitude of discharge

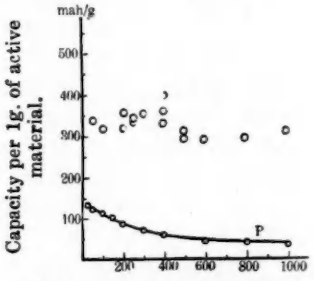

Fig. 5.

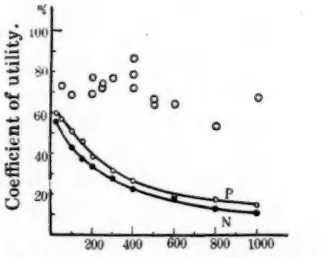

Fig. 6.

current in Fig. 5. The coefficient of utility of the active materials of these electrodes are plotted against the discharge current in Fig. 6. The points indicated by the circlets are the values for the silver oxide electrode.

The curves marked with P are the results of the positive electrodes, and the curve marked with N is the results of the negative electrode of the lead acid cell respectively.

These figures show that the capacities and the utility coefficients of the silver oxide positives are practically independent of the discharge current, and that this electrode has much higher utility coefficient than that of the electrode of lead accumulator.

The watt-hour output of the silver oxide cell and the lead acid cell are compared in Table 3. As seen in this table the watt-hour output of the silver oxide positive is greater than that of the lead peroxide positive so much as about 50%.

Table 3.

	PbO_2 electrode	Ag_2O electrode	
		Example 1	Example 2
Concentration of electrolyte	28% H_2SO_4	20% KOH	20% KOH
Discharge current	200 m. amp.	200 m. amp.	200 m. amp.
Discharge capacity	0.567 a. h.	1.580 a. h.	1.653 a. h.
Coefficient of utility	38.1%	75.2%	78.7%
Mean terminal voltage	1.908 volts	0.984 volts	0.991 volts
w. h. output	1.082 w. h.	1.555 w. h.	1.637 w. h.
Weight per unit w. h. output	6.24 g./w. h.	3.12 g./w. h.	2.96 g./w. h.

The Chemical Reaction Involved in Discharging the Silver Oxide Positive. The discharge characteristic curves of silver positive become in two stages as have already been shown in Fig. 1 and Fig. 4. This can be interpreted by the fact that the chemical reactions of the electrode proceed in two stages expressed by (3) and (4). In order to bring out this fact more clearly, the chemical analysis was made of the active material of electrode in charged state. The electrode which had been subjected to a few cycles of charge and discharge was now fully charged by the current of 200 milliamperes for 72 hours. It was, then, rinsed thoroughly with water in order to be freed from alkali, and the active material was taken out of the grid and made to powder. The sample thus obtained was dried in a deccicator for about 72 hours. The dried sample was dissolved in a small amount of dilute nitric acid and the solution was diluted to 500 c.c. and then was titrated with NH_4CNS solution according to Volhard's method.[3] The results were as follows. Dried sample taken: 5.9745 g. Content of Ag, found: 5.204 g. Ag calculated, assuming the sample to be Ag_2O_2: 5.204 g. Ag calculated, assuming the sample to be Ag_2O: 5.562 g. From this results, we see that the active material of the silver oxide positive in charged state is Ag_2O_2.

The weighed sample of the active material was heated to 120°C. until the weight becomes constant. In the process of this heating the sample changes its colour from bluish black to brown. This corresponds to the decomposition of Ag_2O_2 to Ag_2O and O_2. The brown powder was then heated to dull red heat. The colour now changes readily to silver white. These reactions are expressed by the followings.

$$Ag_2O_2 \xrightarrow{\text{above 100°C.}} Ag_2O + {}^1/_2\,O_2 \xrightarrow{\text{above 300°C.}} 2\,Ag + {}^1/_2\,O_2$$

The results of the chemical analysis are given in Table 4.

Table 4.

Heating bluish black sample to 120°C.	Sample taken		1.9174 g.
	Decrease of weight	Calculated	0.1238 g.
		Found	0.1126
	Content of Ag_2O_2 calculated from the decrease of weight		90.96%

(3) Treadwell, "Lehrbuch der analytische Chemie," II, (1927), 612.

Table 4.—(*Concluded*)

Heating brown sample to dull red.	Sample taken		1.3869 g.
	Decrease of weight	Calculated	0.0957 g.
		Found	0.1029 g.
	Content of Ag_2O calculated from the decrease of weight		107.5%
Heating bluish black sample to 120°C.	Sample taken		3.0008 g.
	Decrease of weight	Calculated	0.1937 g.
		Found	0.1925 g.
	Content of Ag_2O_2 calculated from the decrease of weight		99.33%
Heating brown sample to dull red.	Sample taken		1.3957 g.
	Decrease of weight	Calculated	0.0964 g.
		Found	0.0987 g.
	Content of Ag_2O calculated from the decrease of weight		102.4%

We will consider the relation between the chemical reactions and the utility coefficient of the electrode. Table 5 gives the utility coefficient of an electrode assuming the chemical reaction to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

and

$$Ag_2O \rightarrow 2\,Ag.$$

The values always exceed 100% if they are calculated from the latter equation, while less than 100% from the former one. We know, therefore, that the active material of silver positive in charged state is composed of some higher oxide than Ag_2O.

In conclusion the author wishes to express his hearty thanks to Prof. Sameshima of the Tokyo Imperial University, and Dr. Tiku of the Toyoda Research Laboratory, for their valuable advice on this experiments.

Table 5.

Number of cycle	Discharge hour (h. m.)	Discharge capacity (a. h.)	Coeff. of utility considering chem. reaction to be $Ag_2O_2 \rightarrow 2\,Ag$	Coeff. of utility considering chem. reaction to be $Ag_2O \rightarrow Ag$
1	8.36	2.146	96.4%	192.8%
2	6.08	1.533	68.8	137.6
3	5.39	1.413	63.4	126.8
4	5.50	1.458	65 5	131.0
5	6.38	1.658	74.5	149.0
6	6.43	1.678	75.4	150.8
7	6.46	1.692	76.0	152.0
8	6.35	1.646	74.0	148.0
9	6.17	1.572	70.6	141.2
10	7.06	1.775	79.8	159.6
11	6.49	1.703	76.5	153.0
12	6.28	1.617	72.6	145.2
13	6.12	1.550	69.6	139.2
14	6.10	1.542	69.3	138.6

Summary.

(1) A cell was constructed from the silver positive and iron negative in KOH solution, and the charge and discharge curves of the positive were examined.

(2) It was known that the discharge curve runs in two steps in general, which can be interpreted by assuming that there occurs the following consecutive chemical reactions.

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

(3) The chemical analysis of the active material of charged silver positive supports the above consideration.

(4) The coefficient of utility of the active material of the silver positive is much higher than that of the lead peroxide positive of the lead acid cell.

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The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. VI. The Homogeneity of the Catalytic Action of Oxygen. A Theory of the Oxygen Effect.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received March 31st, 1937.)

While in the absence of oxygen hydrogen bromide adds slowly to allyl bromide (free from peroxides) to give mainly 1,2-dibromopropane (the normal addition), in the presence of oxygen the addition is rapid and the product consists mainly of 1,3-dibromopropane (the abnormal addition). In last paper of this series[1] the authors established that the oxygen effect is caused by molecular oxygen, and pointed out that the next problem was to decide whether the catalytic action of oxygen is homogeneous or heterogeneous.

Kharasch and Mayo[2] observed that the addition of hydrogen bromide to allyl bromide is not influenced by the presence of broken glass pieces and glass wool, showing the reaction is homogeneous. The present authors have confirmed the homogeneity of this reaction by repeating similar experiments.

The ferro-magnetic metals influencing the addition of hydrogen bromide to allyl bromide similarly to oxygen are obviously heterogenous catalysts, because they remain undissolved and unchanged after reaction.

To see whether the active catalyst is dissolved oxygen or adsorbed oxygen the following experiments were carried out. Two Pyrex tubes (capacity about 140 c.c., inner surface area about 280 sq. cm.), one containing a few thin Pyrex tubes with a total surface measuring about 110 sq. cm., were charged each with 24 g. of allyl bromide and 20 g. of hydrogen bromide and 1.5 c.c. of oxygen was admitted at sealing after evacuation. The tubes were placed in the dark at room temperature for three days. They were not shaken but moved now and then. The two additions were effected simultaneously. The total yields of addition (41% for smaller surface area and 43% for greater surface area) and the compositions of the products (1,3-dibromopropane 95% for both) were the same. If oxygen adsorbed on the wall were the active catalyst, a greater

(1) This Bulletin, **12** (1937), 138.
(2) *J. Am. Chem. Soc.*, **55** (1933), 2490.

yield would be expected for the greater surface area in contact with the reacting liquid. But the two experiments resulted similar, thus demonstrating that dissolved oxygen is the active catalyst.

In this way the catalysis by oxygen has been shown to be homogeneous. As recorded in the fifth paper[1], when the amount of oxygen is 1.5 c.c. for 24 g. of allyl bromide and 20 g. of hydrogen bromide in the reaction tube with a capacity 135–140 c.c., the proportion of 1,3-dibromopropane in the product reaches 95%, and any further increase in the amount of oxygen causes no more change in the composition of the product. Even under the assumption that all the oxygen admitted were dissolved in the liquid, 1.5 c.c. correspond to only one molecule of oxygen against 3000 molecules of allyl bromide. How can such a comparatively small amount of oxygen influence so radically the addition of hydrogen bromide to allyl bromide?

The simplest explanation of the oxygen effect might be that oxygen would accelerate the abnormal addition only, say by means of chemical intervention, the normal addition being uninfluenced but conditioned only by the concentrations of the reacting substances. But then it is difficult to reconcile the following findings: The total yield obtained with 1.5 c.c. of oxygen admitted is not more than two to three times that in vacuum in three days' reaction, and in vacuum more than 90% of the product is 1,2-dibromopropane, while, in the presence of oxygen, as much as 95% is 1,3-dibromopropane, although the normal and the abnormal additions might be considered to proceed simultaneously with not very different velocities. Further the proportion of 1,3-dibromopropane should approach asymptotically a certain value as the amount of oxygen increases, whereas the curves obtained are of a quite different type (see the figures of the fifth paper). Moreover, such an explanation can not be compatible with the fact that the total yield of addition increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%): The absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches 1.5 c.c. and thence increases in the same rate as that of 1,3-dibromopropane.

The assumption of a double action of inhibiting the normal addition and accelerating the abnormal addition is none the less inconsistent with the fact, inasmuch as the yield of 1,2-dibromopropane does not keep on decreasing as oxygen increases.

The relation between the amount of oxygen present and the result of addition can be understood if the addition catalysed by oxygen yields

95% 1,3-dibromopropane and 5% 1,2-dibromopropane and in the presence of a sufficient amount of oxygen (1.5 c.c. under the conditions of the experiments) the catalysed addition only takes place.

Thus the authors have been led to advance a theory on the oxygen effect. It is assumed that the oxygen molecule exerts some physical influence on a great number (at least 3000) of molecules of allyl bromide around it. The oxygen molecule may possess a considerably large sphere of influence capable of holding more than 3000 molecules of allyl bromide and a corresponding number of molecules of hydrogen bromide. Otherwise it may influence molecules of allyl bromide colliding with, or coming near to, it, the influenced molecules of allyl bromide keeping their influenced state for a considerably long period—there exist always more than 3000 influenced molecules of allyl bromide per one molecule of oxygen. If allyl bromide has been influenced at all by oxygen in either way, hydrogen bromide adds rapidly to it, 95% of the influenced allyl bromide being transformed into 1,3-dibromopropane and 5% into 1,2-dibromopropane, and thus both dibromopropanes being formed from the influenced molecules of allyl bromide in the presence of a sufficient amount of oxygen. The strength or the freshness of the oxygen influence affects only the rate of addition.

The theory explains satisfactorily the results recorded in the fifth paper: When about 1.5 c.c. of oxygen is admitted under the conditions of the experiments, the whole liquid is just filled with such spheres of influence or all the molecules of allyl bromide exist in the influenced state, and the proportion of 1,3-dibromopropane in the product is 95%. An increase in the amount of oxygen augments the strength or the freshness of the oxygen influence, and an increase in the total yield of the addition is obtained without any further appreciable change in the composition of the product.

It may be considered that the effect of the ferro-magnetic metals is caused by a similar influence. That the normal addition is far inhibited by the presence of these heterogeneous catalysts can not be explained except by the above-mentioned theory. But, the metals are very coarsely divided compared with the dissolved oxygen, and, therefore, their influence must be very strong compared with that of oxygen, corresponding to a very large sphere of influence or to a very long preservation of the influenced state on the part of allyl bromide.

The influence exerted by oxygen and the ferro-magnetic metals is considered to be related closely to the great magnetic susceptibilities with which these substances are endowed. What change occurs in the molecule

of allyl bromide under the influence of oxygen and the ferro-magnetic metals is unknown, but it can be said that the ordinary form preferring the normal addition is changed into an extraordinary form preferring the abnormal addition.

The theory advanced by the authors explains satisfactorily the effect of oxygen and the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. Nevertheless, it may be open to question that the authors have taken it for granted that oxygen and the ferro-magnetic metals have nothing to do with hydrogen bromide, because hydrogen bromide could take the place of allyl bromide in the theory stated above. Further experiments are required before it can be decided whether the substance to be influenced by oxygen and the ferro-magnetic metals is allyl bromide or hydrogen bromide.

In conclusion the authors express their hearty thanks to the Imperial Academy of Japan for a grant. They are also indebted to Prof. M. Katayama and Prof. S. Mizushima for valuable suggestions.

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